Lecture 1: Ideal chains

<table>
<thead>
<tr>
<th><strong>Course outline:</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal chains (Grosberg)</td>
</tr>
<tr>
<td>Real chains (Rubinstein)</td>
</tr>
<tr>
<td>Solutions (Rubinstein)</td>
</tr>
<tr>
<td>Methods (Grosberg)</td>
</tr>
<tr>
<td>Closely connected: interactions (Pincus), polyelectrolytes (Rubinstein), networks (Rabin), biopolymers (Grosberg), semiflexible polymers (MacKintosh)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>This lecture outline:</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers and their uses</td>
</tr>
<tr>
<td>Scales</td>
</tr>
<tr>
<td>Architecture</td>
</tr>
<tr>
<td>Polymer size and fractality</td>
</tr>
<tr>
<td>Entropic elasticity</td>
</tr>
<tr>
<td>Elasticity at high forces</td>
</tr>
<tr>
<td>Limits of ideal chain</td>
</tr>
</tbody>
</table>
Polymer molecule is a chain:

- Polymeric from Greek poly-merēs having many parts; First Known Use: 1866 (Merriam-Webster);
- Polymer molecule consists of many elementary units, called monomers;
- Monomers - structural units connected by covalent bonds to form polymer;
- N number of monomers in a polymer, degree of polymerization;
- $M = N \times m_{\text{monomer}}$ molecular mass.

Examples: polyethylene (a), polysterene (b), polyvinyl chloride (c)...

... and DNA
Another view:
Scales:

- $k_B T = 4.1 \text{ pN} \cdot \text{nm}$ at room temperature ($24^\circ \text{C}$)
- Breaking covalent bond: $\sim 10000 \text{ K}$; bonds are NOT in equilibrium.
- “Bending” and non-covalent bonds compete with $k_B T$
- Monomer size $b \sim \text{Å}$
- Monomer mass $m$ - from 14 to ca 1000
- Polymerization degree $N \sim 10$ to $10^9$
- Contour length $L \sim 10 \text{ nm to } 1 \text{ m}$
# Polymers in materials science

(e.g., alkane hydrocarbons -\((\text{CH}_2)\)-)

<table>
<thead>
<tr>
<th># C atoms</th>
<th>1-5</th>
<th>6-15</th>
<th>16-25</th>
<th>20-50</th>
<th>1000 or more</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ 25°C and 1 atm</td>
<td>Gas</td>
<td>Low viscosity liquid</td>
<td>Very viscous liquid</td>
<td>Soft solid</td>
<td>Tough solid</td>
</tr>
<tr>
<td>Uses</td>
<td>Gaseous fuels</td>
<td>Liquid fuels and solvents</td>
<td>Oils and greases</td>
<td>Candles and coatings</td>
<td>Bottles...</td>
</tr>
<tr>
<td>Examples</td>
<td>Propane</td>
<td>Gasoline</td>
<td>Motor oil</td>
<td>Paraffin wax</td>
<td>Polyethylene</td>
</tr>
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![Propane](image1.png) ![Gasoline](image2.png) ![Motor oil](image3.png) ![Paraffin wax](image4.png)
### Polymers in living nature

<table>
<thead>
<tr>
<th></th>
<th>DNA</th>
<th>RNA</th>
<th>Proteins</th>
<th>Lipids</th>
<th>Polysaccharides</th>
</tr>
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<tbody>
<tr>
<td>N</td>
<td>Up to $10^{10}$</td>
<td>10 to 1000</td>
<td>20 to 1000</td>
<td>5 to 100</td>
<td>gigantic</td>
</tr>
<tr>
<td>Nice physics models</td>
<td>Bioinformatics, elastic rod, charged rod, helix-coil</td>
<td>Secondary structure, annealed branched, folding</td>
<td>Proteomics, randomdesigned heteropolymer, HP, funnels, ratchets, active brushes</td>
<td>Bilayers, liposomes, membranes</td>
<td>??? Someone has to start</td>
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#### Uses

<table>
<thead>
<tr>
<th>DNA</th>
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<th>Polysaccharides</th>
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<tr>
<td><img src="image1" alt="DNA" /></td>
<td><img src="image2" alt="RNA" /></td>
<td><img src="image3" alt="Proteins" /></td>
<td><img src="image4" alt="Lipids" /></td>
<td><img src="image5" alt="Polysaccharides" /></td>
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<table>
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<tr>
<th>Molecule</th>
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<td><img src="image6" alt="Molecule" /></td>
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Polymer properties depend on...

- Chemical composition of a monomer;
- Degree of polymerization, $N$;
- Flexibility;
- Architecture;
- \textcolor{red}{Homo}polymer versus \textcolor{green}{hetero}polymer.
Architecture

- linear
- comb
- star
- ring
- randomly branched
- network
Architecture cont’d
Homo- vs. Hetero

Homopolymer consists of monomers of just one sort:


Heteropolymer (copolymer) has two or more monomer species:


alternating


random


B B B B B

B B B B B

B B B B B

A-A-A-B-B-B-B-B-B-B-B-B-B-B

triblock


A-A-A-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B

multiblock

Flexibility

- Sufficiently long polymer is never straight

- Different polymers bend differently:
Polyethylene: bond length $l \cong 1.54\text{Å}$, tetrahedral angle $\theta \cong 68^\circ$

Rotation isomers:
- Torsion (measured in angle $\phi$) - main source of polymer flexibility.

$\Delta \varepsilon \sim k_B T$

Torsion (measured in angle $\phi$) - main source of polymer flexibility.
Elastic flexibility:

- Within one rotamer, $\Delta E \sim \phi^2$ - Hook’s law.
- Many polymers have no freedom to explore rotational isomers, e.g., two strands.
- Elastic rod model:

$$E = \int_0^L \left[ \frac{1}{2} \kappa \dddot{r}^2(s) + \frac{1}{2} \alpha \dot{\phi}^2(s) \right] ds$$

$s$ $\mathbf{r}(s)$ $\dot{\mathbf{r}}(s)$ "velocity"
How much is polymer bent?

- How much is polymer bent?
- What is its size $R$, given $N$?
- Can we measure it?
- How/why is it important?
- How does it depend on conditions, e.g., temperature?
Polymer Size

Monomer size $b \sim 0.1\text{nm}$; Number of monomers $N \sim 10^2 - 10^{10}$;
Contour length $L \sim 10\text{nm} - 1\text{m}$;
Depending on how much polymer is bent, its overall size $R$ varies widely and depends on solvent quality.

Long-range repulsion $R \sim L \sim bN$  
Good solvent $R \sim bN^{3/5}$  
$\theta$-solvent $R \sim bN^{1/2}$  
Poor solvent $R \sim bN^{1/3}$
Astronomical Variations of Polymer Size

Increase monomer size by a factor of $10^8$: $b \sim 1\text{cm}$; let $N=10^{10}$.

**Poor solvent**

$R \approx bN^{1/3} \approx 20\text{m}$

**θ-solvent**

$R \approx bN^{1/2} \approx 1\text{km}$

**Good solvent**

$R \approx bN^{3/5} \approx 10\text{km}$

**Long-range repulsion**

$R \approx L \approx bN \approx 10^5 \text{ km}$
Ideal polymer vs. ideal gas

- Strong dependence of polymer size on environment/solvent conditions suggests a big role of interactions.
- Ideal polymer has no interactions between monomers, except between neighbors along the chain.
- Just like ideal gas may have all sorts of rotations and vibrations in the molecule, but no interactions between molecules.
- Like ideal gas is the most useful idealization in statistical mechanics, so is the ideal polymer.
- Ideal chains are good models for polymer melts, concentrated solutions, and dilute solutions at θ-temperature.
Ideal chain: no interactions between monomers if they are not neighbors along the chain, even if they approach one another in space.

Conformation of an ideal chain is fully specified by the set of bond vectors \( \{y_i\} \)

End-to-end vector of an ideal chain: \( \mathbf{R} = \sum_{i=1}^{N} y_i \)

Averaged value of end-to-end vector is zero: \( \langle \mathbf{R} \rangle = 0 \), because \( -\mathbf{R} \) is equally likely as \( \mathbf{R} \)
Ideal chain size: mean squared end-to-end distance

Ideal chain: no interactions between monomers if they are not neighbors along the chain, even if they approach one another in space.

Conformation of an ideal chain is fully specified by the set of bond vectors \( \{y_i\} \)

End-to-end vector of an ideal chain: \( \mathbf{R} = \sum_{i=1}^{N} y_i \)

Since averaged value of end-to-end vector is zero: \( \langle \mathbf{R} \rangle = 0 \), to estimate the size we want to compute \( \langle | \mathbf{R} | \rangle \) or \( \langle \mathbf{R}^2 \rangle \)

\[
\langle \mathbf{R}^2 \rangle = \langle \mathbf{R} \cdot \mathbf{R} \rangle = \left\langle \left( \sum_{i=1}^{N} y_i \right) \cdot \left( \sum_{j=1}^{N} y_j \right) \right\rangle = \sum_{i,j=1}^{N} \langle y_i \cdot y_j \rangle = l^2 \sum_{i,j=1}^{N} \langle \cos \theta_{ij} \rangle
\]

Freely-jointed chain or lattice model:

\[
\langle \cos \theta_{ij} \rangle = 0 \text{ except when } i = j \quad \Longrightarrow \quad \langle \mathbf{R}^2 \rangle = Nl^2
\]
Ideal chain size: mean squared end-to-end distance

For ideal chains, one can show that there are no long-range correlations between bond directions:

\[ \lim_{|i-j| \to \infty} \langle \cos \theta_{ij} \rangle = 0 \]

\[ C'_i = \sum_{j=1}^{N} \langle \cos \theta_{ij} \rangle \text{ rapidly converges at large } N \]

\[ \langle R^2 \rangle = l^2 \sum_{i,j=1}^{N} \langle \cos \theta_{ij} \rangle = l^2 \sum_{i=1}^{N} C'_i = C_N N l^2 \approx C_\infty N l^2 \]

For example, freely-rotating chain: \[ C_\infty = \frac{1+\cos \theta}{1-\cos \theta} \]

Specific flexibility mechanism (rotational isomers etc) is hidden in characteristic ratio \( C_\infty \);
see P.Flory, Statistical Mechanics of Chain Molecules.
Ideal chain size: worm-like chain
(Kratky and Porod model)

$$R = \sum_{i=1}^{N} y_i \implies R = \int_0^L \dot{r}(s)ds$$

**Key argument:**

$$\langle \cos \theta_{s_1,s_3} \rangle = \langle \cos \theta_{s_1,s_2} \rangle \langle \cos \theta_{s_2,s_3} \rangle$$

**Proof:** consider \( \dot{r}_1 \cdot \dot{r}_3 = \dot{r}_1^\perp \dot{r}_3^\perp + \dot{r}_1^\parallel \cdot \dot{r}_3^\parallel \), where parallel and perpendicular components are taken with respect to \( \dot{r}_2 \). Perpendicular components vanish upon averaging.

**Consequence:**

$$\langle \cos \theta(s-t) \rangle = e^{-|s-t|/l}$$

$$\langle R^2 \rangle = \int_0^L \int_0^L \langle \dot{r}(s) \cdot \dot{r}(t) \rangle dsdt = \int_0^L \int_0^L \langle \cos \theta(s-t) \rangle dsdt = \int_0^L \int_0^L e^{-|s-t|/l} dsdt$$

$$\langle R^2 \rangle = 2l^2 \left[ \frac{L}{l} - 1 + e^{-L/l} \right] = \begin{cases} L^2 & \text{if } L \ll l \\ 2Ll & \text{if } L \gg l \end{cases}$$

**Problem:** relate length \( l \) to rigidity constant \( \kappa \) in \( \Delta E = \int_0^L \frac{1}{2} \kappa \ddot{r}^2(s)ds \).
Universal description of ideal polymer

Construct **equivalent freely jointed chain** with the same mean squared end-to-end distance \( \langle R^2 \rangle \) and the same contour length \( L \) as actual polymer. It consists of \( N \) effective, or Kuhn, segments, each of length \( b \), such that:

For chain of \( n \) bonds of length \( l \) each:

\[
\langle R^2 \rangle = N b^2 = C_\infty n l^2
\]
\[
N b = n l
\]

Kuhn length and # of effective segments are

\[
b = C_\infty l
\]
\[
N = n / C_\infty
\]

Worm-like chain, total length \( L \), persistence \( l \):

\[
\langle R^2 \rangle = N b^2 = 2 L l
\]
\[
N b = L
\]

Kuhn length and # of effective segments are

\[
b = 2 l
\]
\[
N = L / 2 l
\]

Equivalent freely jointed chain differs from the actual polymer on length scales of Kuhn segment \( b \) or smaller, but has the same physical properties on large scales.
Reverse the question of polymer size: how many monomers are there within radius $r$?

- If $r$ is greater than Kuhn segment, $r > b$, then sub-coil of $g$ monomers has size $R(g) \sim g^{1/2}b$;
- Therefore, within radius $r$ we expect $m(r) \sim (r/b)^2$ monomers.
Counting “atoms” in regular objects

- For a 3D object, \( m \sim r^3 \)
- For a 2D object, \( m \sim r^2 \)
- For a 1D object, \( m \sim r^1 \)

Mathematically:

\[
m(r) = \begin{cases} 
\frac{4\pi}{3} r^3 & \text{if } r < H \\
\pi r^2 & \text{if } r \gg H 
\end{cases}
\]

\[
m(r) = \begin{cases} 
\frac{4\pi}{3} r^3 & \text{if } r < H \\
\frac{2r}{H} & \text{if } r \gg H 
\end{cases}
\]
Koch curve: example of a fractal

\[ r_1 = 3r_2 \text{ and } m(r_1) = 4m(r_2), \text{ in general } m(3r) = 4m(r) \]

This has the solution in the form of power law \( m(r) \sim r^{d_f} \), with \( 3^{d_f} = 4 \) or \( d_f = \frac{\ln 4}{\ln 3} \approx 1.26 \).

\[ m \sim r^{d_f} \]

\( d_f \) - fractal dimension

We can either increase “observation field” \( r \), or decrease the size of elementary “atom”
Polymeric fractals

For ideal chain, \( m(r) \sim (r/b)^2 \); that means, ideal polymer has fractal dimension \( d_f = 2 \).

Scaling exponent \( \nu = 1/d_f = 1/2 \) for ideal polymer.

We will see later that in a good solvent \( d_f = 5/3 \) and \( \nu = 3/5 \).

Ideal coil can be viewed as \( N/g \) blobs of \( g \) segments each. Blob size is \( x \sim bg^{1/2} \), therefore \( R \sim bN^{1/2} \sim x(N/g)^{1/2} \).

**Problem:** consider polymer adsorbed on a 2D plane. What are the consequences of the fact that \( d_f = D \)?
Radius of gyration

End-to-end distance is difficult to measure (and it is ill defined for, e.g., rings or branched polymers). Better quantity is gyration radius:

\[ R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{R}_i - \mathbf{R}_{cm})^2 \]

Where position vector of mass center is

\[ \mathbf{R}_{cm} = \frac{1}{N} \sum_{i=1}^{N} \mathbf{R}_i \]

There is theorem (due to nobody lesser than Lagrange) which says that

\[ R_g^2 = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{R}_i - \mathbf{R}_j)^2 \]

**Exercises:** (1) Prove Lagrange theorem; (2) Prove that for ideal linear chain \( R_g^2 = Nb^2/6 \); (3) Prove that for ideal ring \( R_g^2 = Nb^2/12 \)
Entropic elasticity

Optical tweezers experiment

How much force should we apply to achieve end-to-end distance $R$?
Pincus blob argument

Every piece of the chain is under the same tension $f$. This tension cannot be important for the chain at the length scale smaller than $\xi$ such that $f\xi \sim k_B T$. This scale $\xi$ is called Pincus blob size. If $\xi$ is larger than Kuhn segment $b$, universal statistics should apply. Then the number of segments per blob is such that $b^2 g \sim \xi^2$.

The condition $\xi > b$ translates into $f < k_B T/b$. At the same time, blob must be smaller than the coil itself, and $\xi < R$ becomes $f > k_B T/b\sqrt{N}$. In this wide range of forces $k_B T/b > f > k_B T/b\sqrt{N}$ we can proceed.

Chain of blobs is fully stretched, which means $R \sim \xi N/g$, or

$$R \sim \frac{Na^2}{k_B T} f,$$

or $f \sim \frac{k_B T}{Nb^2} R$.

This looks “almost” like Hooke’s law! But since force is the derivative of free energy, we get the latter and, as a prize, the probability distribution of $R$:

$$F(R) \sim k_B T R^2 / Nb^2 \quad \text{and} \quad P(R) \sim \exp \left[ \frac{F(R)}{k_B T} \right] \sim \exp \left[ -\frac{3R^2}{2Nb^2} \right].$$

The coefficient $3/2$ in the last formula cannot be established by this argument.

Gauss distribution of $R$ follows directly from Central Limit Theorem
What if we pull harder?

Gaussian theory is satisfactory only up to about 0.1pN.

Non-universal elasticity at higher forces

**Freely-jointed:** Entropic price of confining one segment into a tube is about $k_B \ln(D^2/\ell^2)$, or $\Delta S = N k_B \ln(D^2/\ell^2)$. How is $D$ related to end-to-end distance $R$? For each segment, its projection along the tube axis is $\sqrt{\ell^2 - D^2} \approx \ell - D^2/2\ell$ (since $D \ll \ell$). Therefore, $R \approx N (\ell - D^2/2\ell) = L - LD^2/2\ell^2$. Then

$$\Delta F \sim -k_B T \ln \left(1 - \frac{R}{L}\right) \quad \text{and} \quad f \sim \frac{k_B T}{L - R}.$$

**Worm-like:** Curvature radius $\rho$ of the arc is about $\rho \sim \lambda^2/D$. Bending energy of the arc $E_{bend} \sim k_B T b \lambda/\rho^2$ being about $k_B T$ yields Odijk length:

$$\lambda \sim b^{1/3} D^{2/3}.$$

Worm-like chain hits the tube walls more frequently, in more places, than freely-jointed chain, since $\lambda \ll b$. End-to-end distance $R$ is geometrically related to $\lambda$:

$$R \approx L - LD^2/2\lambda^2, \text{ or } R - L \approx -L\lambda/b.$$

Confinement entropy is of order unity per Odijk length:

$$\Delta F \sim -k_B T \frac{L^2}{(L - R)b} \quad \text{and} \quad f \sim \frac{k_B T L^2}{(L - R)^2 b}.$$
From Langevin to Marko-Siggia

• Exact formula for freely-jointed chain:

\[ R = N \ell \left( \frac{e^\xi + e^{-\xi}}{e^\xi - e^{-\xi}} - \frac{1}{\xi} \right) \]

where

\[ \xi = \frac{f \ell}{k_B T} \]

• Very accurate formula for worm-like chain:

\[ f = \frac{k_B T}{2b} \left[ \frac{L^2}{(L-R)^2} - 1 + \frac{4R}{L} \right] \]

Compare: Einstein and Debye theories of heat capacity of a solid
Chains Get Softer Under Tension

Linear deformation regime ends at $f \sim k_B T / b$.

Problem: Why is there a cross-over from semi-flexible (worm-like) chain to flexible (freely-jointed) chain with increasing tension at $f_c \sim k_B T K/l$?
Pair Correlations of an Ideal Chain

Number of monomers within range $r$

$$m \approx \left( \frac{r}{b} \right)^2$$

Probability of finding a monomer at a distance $r$ from a given one

$$g(r) \approx \frac{m}{r^3} \approx \frac{1}{rb^2}$$

Pair correlation function for a D-dimensional fractal with $m \sim r^D$

$$g(r) \approx \frac{m}{r^3} \sim r^{D-3}$$
Scattering provides ensemble average information over wide range of scales

Light Scattering

Alan Hurd
Summary of Ideal Chains

- No interactions except along the chain
- Equivalent Kuhn chain
- Mean square end-to-end: \( \langle R^2 \rangle = Nb^2 \)
- Mean squared gyration radius: \( \langle R_g^2 \rangle = \frac{Nb^2}{6} \)
- Probability distribution: \( P_{3d}(N, \bar{R}) = \left( \frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right) \)
- Free energy: \( F = \frac{3}{2} kT \frac{\bar{R}^2}{Nb^2} \)
- Entropic "Hook's Law": \( \tilde{f} = \frac{3kT}{Nb^2} \bar{R} \)
- Pair correlation function: \( g(r) = \frac{3}{\pi rb^2} \)
- Nonlinear elasticity at high forces
Mayer f-function

Effective interactions potential between two monomers in a solution of other molecules.

Relative probability of finding two monomers at distance $r$

$\exp(-U/kT)$

Mayer f-function

$$f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1$$

Excluded volume

$$v = -\int f(\vec{r}) d^3r$$
Classification of Solvents

\[ v = -\int f(\vec{r})d^3r \]

**Athermal, high T**

- Good solvent, repulsion dominates: \[ f \quad \begin{array}{c} b \ \ \ \ r \end{array} \quad 0 < v < b^3 \]

- \(\theta\)-solvent, repulsion compensates attraction: \[ f \quad \begin{array}{c} \ \ \ \ r \end{array} \quad v = 0 \]

- Poor solvent, attraction dominates: \[ f \quad \begin{array}{c} \ \ \ \ r \end{array} \quad v < 0 \]

Typically, but not always, repulsion dominates at higher, and attraction -- at lower temperatures.
Pair interaction dominance:

- In ideal coil, $R \sim bN^{1/2}$. Monomer volume fraction $\phi \sim Nb^3/R^3 \sim N^{-1/2} << 1$

- The number of pair contacts $N_\phi \sim N^{1/2} \gg 1$; pair collisions are important.

- The number of triple contacts $N_\phi^2 \sim 1$; they become important only if chain collapses.

- Higher order are unimportant unless strong collapse.